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Superiority of intrinsic biopolymeric constituents in briquettes of lignocellulosic crop residues over wood: A TG-diagnosis

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ABSTRACT

The paper proves that briquettes of lignocellulosic crop residues have higher activation energy levels of intrinsic biopolymers as compared to these energy levels in wood, especially in context with the hemicellulosic and cellulosic segment. Binderless briquettes made of residues from pigeon pea and soybean crops were analyzed in comparison with wood. Thermal decompositions of these biofuels were experimented by thermogravimetry under pyrolysis environment and the transitions of the thermogravimetric signals were explained. Popular isoconversional kinetics method, namely integral Ozawa-Flynn-Wall was used to evaluate and compare the activation energies. Kinetics analyzed that wood was thermally weaker than the briquettes.

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1. Introduction

Wood has been in use for thermal energy generation since long. Almost all designs of thermal devices are based on the thermal degradation behaviors of the wood. In view of the deforestation, the emphasis on the use of alternative biofuel increased and several options to obtain the biofuel to replace or supplement the wood were searched. The search was basically for the biofuel better or near to the wood. The briquette of agro-residues is one of the best options in this context.

Briquette is compact, uniform, solid bio-fuels from agro-residues to increase the flexibility of utilizing the agro-residues, for energy generation [1–3]. The main concept for conversion of agro-residues in briquettes is to substitute the wood in thermal energy devices and to utilize the agro-residues [4,5]. General perception is that the wood is strong material in the thermal degradation as compared with other biomass. The briquettes are formed from the loose crop residues and therefore, their thermal degradation is also thought to be similar to their raw material.

Agro-residues, especially crop residues, are available in a substantial quantity after the harvest of the crop which can be used as a sustainable renewable energy source [6]. The main limitation in utilization of crop residues as biofuel in energy systems is their low bulk density <200 kg/m^3 [1–3]. For biomaterial having low bulk densities, the management (handling, transportation and storage) of crop residues becomes very difficult. Further, due to light weight, irregular shape and size, the crop-residues create the chocking and blockage in the reactors of bioenergy gadgets. Therefore, the uniformly sized solid biofuels having high density (until 1200 kg/m^3) is desirable which can be produced using the briquetting process and such type of briquetted biofuel can be conveniently used for energy generation [1–3,6,7]. The briquettes can be produced using some binder or without a binder. Teixeira et al. (2010) published their work on, hand pressed briquettes using charcoal mixed with a binder (starch) obtained from cassava flour (a tropical root) [8]. In the present article, the binder-less briquettes are in discussion wherein no binder was used and the biopolymer constituents of crop residues took part in the binding process of biomolecules to create the briquettes. In binderless briquetting, biopolymeric lignin present in the crop residues experiences the briquetting stresses and acts like a glue to bind the different components of the biomaterial to form the briquette. It is established fact that lignocellulosic crop residues can be briquetted by changing the process parameters [1–9], e.g., sawdust, bagasse, mustard stalk, groundnut shell, pigeon pea stalk, soybean straw, cotton and char, etc.

Abbreviations: TGA, thermogravimetric analysis; PB, briquettes made from pigeon pea stalk; SB, briquettes made from soybean straw; OWF, Ozawa-Flynn-Wall.

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There are three types of briquetting systems in the market, namely i) Screw-press type, ii) Piston-press (die-punch) type and iii) Rotary dies and roller type [2,3,5]. In piston-press type systems [5], a piston (ram) exerts heavy pressure in regular pulses on the raw biomaterial and forces it through a die. Due to exerted pressure, the raw biomaterial is heated, and the loose crop residues are converted in the briquettes. In case of screw press type systems [8], a conveyer screw exerts heavy continuous pressure on biomaterial. This screw conveys the raw biomaterial to a die where the briquettes are produced. The piston-press consumes less energy per unit output [2,3] as compared to screw press system.

Lignocellulosic crop-residues consist of biopolymeric cellulose, hemicellulose, and lignin. In briquetting, the raw bio-material is pressed as high as 100 MPa and temperatures may exceed 200 °C in the die-region. This stress conditions are enough to soften the lignin [2,3]. Actually, all biopolymeric constituents experience modification in their configuration which can reliably be investigated in-depth using the thermogravimetric analysis (TGA). In TGA, the biomaterial is heated in confined chamber and the weight during the reduction in thermal decomposition is measured.

Thermal decomposition can be considered to occur in major four stages, namely moisture release, hemicellulose decomposition, cellulose decomposition and lignin decomposition, as mentioned by Vasile et al. (2011) [10]. Caballero et al. (1997) and López-González et al. (2013) also stated that thermal degradation of lignocellulosic biomaterials may be taken as the sum of independent decompositions of their main components [11,12]. Ledakowicz and Stolarek, (2002) suggested that the evolution of each volatile can be considered as a single first order reaction assuming that the constituents of bio-material are evolved by independent parallel reactions [13]. According to Sanchez-Silva et al. (2012), hemicellulose has a random and amorphous structure possessing less strength than cellulose. which has a crystalline and strong structure. They added that lignin showed the highest thermal stability, decomposing in a wide range of temperatures (200–700 °C) and the DTG profile of lignin was the flattest [14]. Decomposition of lignin is stated as a most complex process because the lignin is heavily cross-linked highly branched biopolymer [14].

The goal of this study is to compare the thermogravimetric behaviors of wood with briquetted biofuel generated from two different kinds of crop residues. The popular methods of evaluation of kinetics during thermal decay are Friedman method, Coats-Redfern method, Kissinger–Akahira–Sunose (KAS) method, Ozawa-Flynn-wall (OFW) [15–17]. Friedman method is a differential method, whereas Coats-Redfern, Kissinger–Akahira–Sunose (KAS) and Ozawa-Flynn-Wall methods are integral iso-conversional method [18].

2. Materials and methods

The raw materials for investigation were residues of pigeon pea crops (stalks) and soybean crop (straw) and local wood (local name: su-babool). Soybean crop (*Glycine max* (*L.*) *Merr.*) is an important crop in the central region (Madhya Pradesh) of the India [19]. Generally, combine harvesters are used for harvesting. Combine harvesters leaves the threshed residues in the field, itself. After combining, the residues were collected for this study within one week of the harvesting. Raw soybean straw and briquetted biofuel had moisture contents of 8–12 % (dry weight basis). Raw soybean straw was powdered so that it could be briquetted. The particle distribution of raw powdery biomaterial was <1.7 mm (2%), 1.4–1.7 mm (14%), 0.70–1.4 mm (16%), 0.4–0.7 (37%), 0.2–0.4 mm (16%) and >0.2 mm (15%). The bulk densities of powdered soybean straw and briquette were ~255 and ~660 kg/m^3, respectively, achieving the densification level of 2–3 times. Ash contents of samples of the briquettes and soybean straw were 5% and 2%, respectively.

The characteristics and thermogravimetric information for pigeon pea (*Cajanus cajan*) stalk and their briquettes is available in recently published papers [20,21]. The characterization of wood (*Prosopis juliflora*) samples and raw thermogravimetric data are available in earlier writings [22–24]. The comparative thermogravimetric transitions and kinetics of wood are analyzed and discussed in the present article.

A commercial piston-press (rated capacity 500 kg/h; rated power 35 kW; installed at Agricultural Energy and Power Division, Central Institute of Agricultural Engineering, Bhopal, India) briquetting machine was used to form the briquettes of pigeon pea stalk and soybean stalk [24,25]. Piston-press exerted heavy pressure (110 ± 30 Mpa) on raw powdery crop-residues to form briquettes due to that the temperature at the die crossed 200 °C. Thus, crop residues experienced stresses (temperature and heavy pressure) in a semi-confined environment during the briquetting.

Thermogravimetry was conducted in the thermogravimetric analyzer (Model: pyris-6; Make: Perkin Elmer). Three types of biomaterials under evaluation were two kinds of briquette samples, briquette of the pigeon pea stalk and briquette of the soybean straw, and local wood. Three samples of each biomaterial namely soybean briquette, pigeon pea briquette and wood (*P. juliflora*) were taken for TGA. The TGA-temperature was kept constant at 35 °C for 2 min and then, the temperature was raised at different heating rates (β) from 35 °C to 1000 °C in pyrolysis conditions under nitrogen ambient. For thermogravimetry, four β (10, 20, 30 and 40 °C/min) were used which were essential to apply the isoconversional kinetics methods. In thermogravimetry, we obtain the data with respect to weight loss (%) versus reaction temperature or time (thermogram). The first order derivative (decomposition rate profile) of the thermogram is a plot of the weight loss rate versus temperature or time, i.e., in respect of the degradation rate, %/min. The first order derivative is also known as “differential thermogram (DTG)”. The data with respect to temperature, degradation rates can easily be linked with the conversion fraction (α). Conversion fraction is a measure of fraction of mass under the thermal degradation at a particular instant. The conversion fraction (α) is defined as $\alpha = (wi - wt)/(wi - w\infty)$; where; the wi, wt and w∞ are the masses of bio-material at initial, instantaneous and final stages of decomposition, respectively. By doing the conversion fraction based comparison of two or more biomasses, the effect of residual mass on thermogravimetric interpretations can be avoided and the chances of error due to residues remaining at the end of thermal degradation minimizes. For comparison, the thermogravimetric kinetics of wood and briquettes was evaluated using integral Ozawa-Flynn-Wall (OFW) isoconversional kinetic method. Ozawa-Flynn-Wall method uses the equation [18] as given below;

$$\ln(\beta) = \ln\left(\frac{AE}{R}\right) - \ln g(\alpha) - 5.3305 - 1.052\left(\frac{E}{RT}\right) \tag{1}$$

$$g(\alpha) \equiv \int_{\alpha i}^{\alpha 0} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \cdot \int_{Ti}^{To} e^{\left(\frac{-E}{RT}\right)} \cdot dT = \frac{A}{\beta} \cdot I(E,T) \tag{2}$$

where; E = activation energy; T = reaction temperature (absolute); t = reaction time, f(α) = reaction model; A = Arrhenius pre-exponential factor, R = Universal gas constant; I(E,T) = temperature integral.

Ozawa-Flynn-Wall curves (ln(β) versus 1/T) were drawn at all β for all the three biomaterials. The isoconversional levels were selected at α-value equal to 0.01, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90 and 0.95. Ozawa-Flynn-Wall points (1/T, ln(β)) were extracted at each selected α-level for all experimented β. The isoconversional kinetic lines (1/T versus ln(β)) were drawn at each selected α-level. The activation energies were calculated from the slope ($-1.052^{*}E/R$) of OFW kinetics lines obtained at different selected values of α-level.

3. Results and discussion

Thermal stability of intrisic biopolymeric components of briquettes over local wood (*P. juliflora*) is highlighted in this paper. The α-domain thermograms of the wood and two types of briquettes, pigeon pea stalk briquette (PB) and soybean straw briquette (SB) are shown in Fig. 1. The thermal decomposition rates at all experimented β are given in Fig. 2. The decomposition rates were negative because the mass is reduced during the thermal degradation. For clarity, Fig. 3 shows the region of lignin degradation and the gaseous evolution of Fig. 2. Fig. 1 shows the remarkable deviations in the α-regions 0.05–0.25 and 0.70–1.00. The α-region 0.05–0.10 was related to moisture evaporation and from 0.10 to 0.25 is related with hemicellulosic degradation (Fig. 2). The region of α-domain >0.7 was linked with the lignin degradation and gaseous evolution. The dehydration in all material ended until α-value of 0.1. In case of soybean straw briquette the hemicellulosic signals were not clear. Hemicellulose signals [10–14,20,21,26–31] in pigeon pea briquettes were falling in the α-range of 0.1–0.4 whereas in case wood these signals were at slightly lower α-range, showing that the hemicellulosic decay in wood occurred earlier than the decay in the PB.

The highest peaks in all thermograms were related to cellulosic degradation [10–14,20,21,26–31]. The α-location wise cellulose signals were PB > SB > W at 10 °C/min, PB > SB ≥ W at 20 °C/min, PB > W ≥ SB at 30 °C/min and PB > SB > W at 40 °C/min. These trends indicated that the briquettes were thermally harder than wood. The hemicellulosic decomposition rates were less than cellulosic decomposition in the case of each biomaterial under evaluation. Vasile et al., 2011 indicated that hydrocarbons, aldehydes, ketones, acids, alcohols and others were generated by the primary pyrolysis of hemicelluloses and cellulose [10]. According to López-González et al., 2013, during cellulose decomposition, a complex set of reactions as denitration and deacetylation, scission of O—N, C—O, C—C and C—H bonds might take place [12]. During hemicellulosic decomposition, the breakdown of C—O—C and C—C bonds were possible [12].

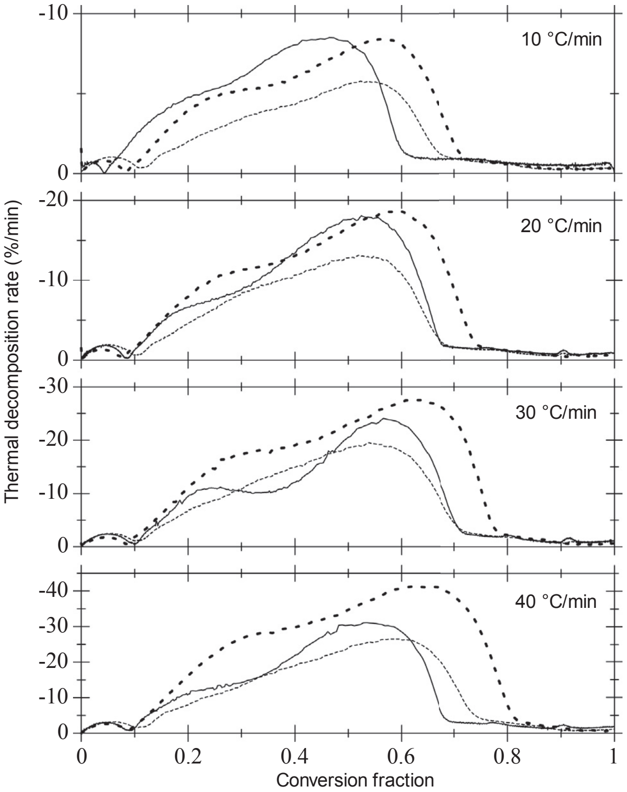

Fig. 2. Decomposition rate profile of wood (solid lines) and two types of briquettes (dark dashed lines are pigeon pea stalk briquettes and light dashed lines are soybean straw briquettes).

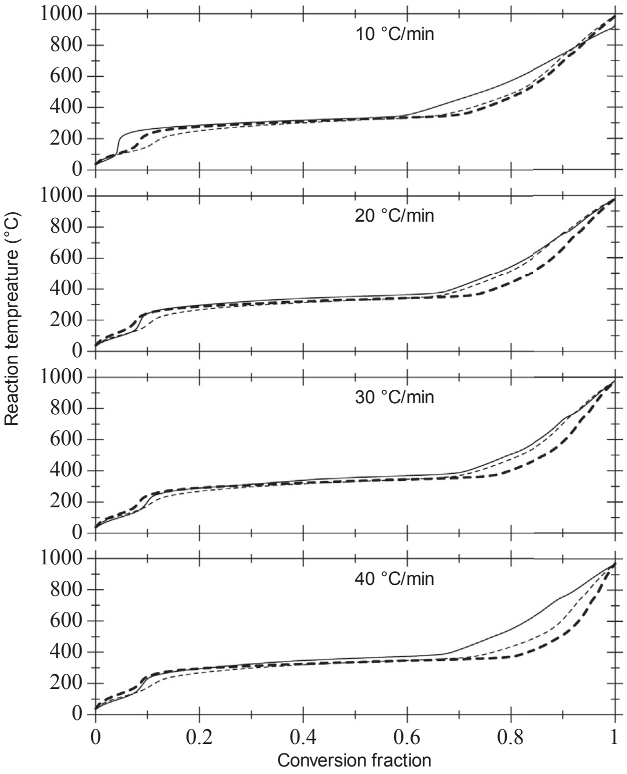

Fig. 1. Conversion fraction versus reaction temperature plots for wood (solid lines) and two types of briquettes (dark dashed lines are pigeon pea stalk briquettes and light dashed lines are soybean straw briquettes).

The lignin [20,21,27–32] related peaks were visible (Fig. 3) only in wood, whereas SB did not show the distinct signals of lignin. The dull and weak presence of lignin was seen in SB at $\alpha = 0.78$ at 20 °C/min and at 0.87 at 40 °C/min. The lignin TG-signals in wood were dull at 10 °C/min located at $\alpha = 0.75$. At $\beta = 20$, 30, 40 °C/min, the lignin signals were at $\alpha = 0.76$, 0.80 and 0.77, respectively. PB showed flat signals of lignin located at $\alpha = 0.81$, 0.83, 087 and 0.89 at $\beta = 10$, 20, 30 and 40 °C/min, respectively. In general, the lignin signal fell at higher α-location in the briquetted biofuel then their location in the wood showing the existence of hard lignin in the briquettes. The lignin decomposition is expected to impact a three-dimensional structure consisting of phenylpropane coupled with C—C or C—O—–C bonds whose activity covers a wide range of temperatures as suggested by López-González et al. (2013) [12]. The dominant volatiles released from lignin pyrolysis are the phenols and alcohols as stated by López-González et al. (2013) [12].

Minor peaks were seen at $\alpha \geq 0.90$ which were ascribed to the release of hydrogen and methane (gaseous evolution) due to the secondary charring process [33–35]. Broadly, α-region 0.89–1.00 is

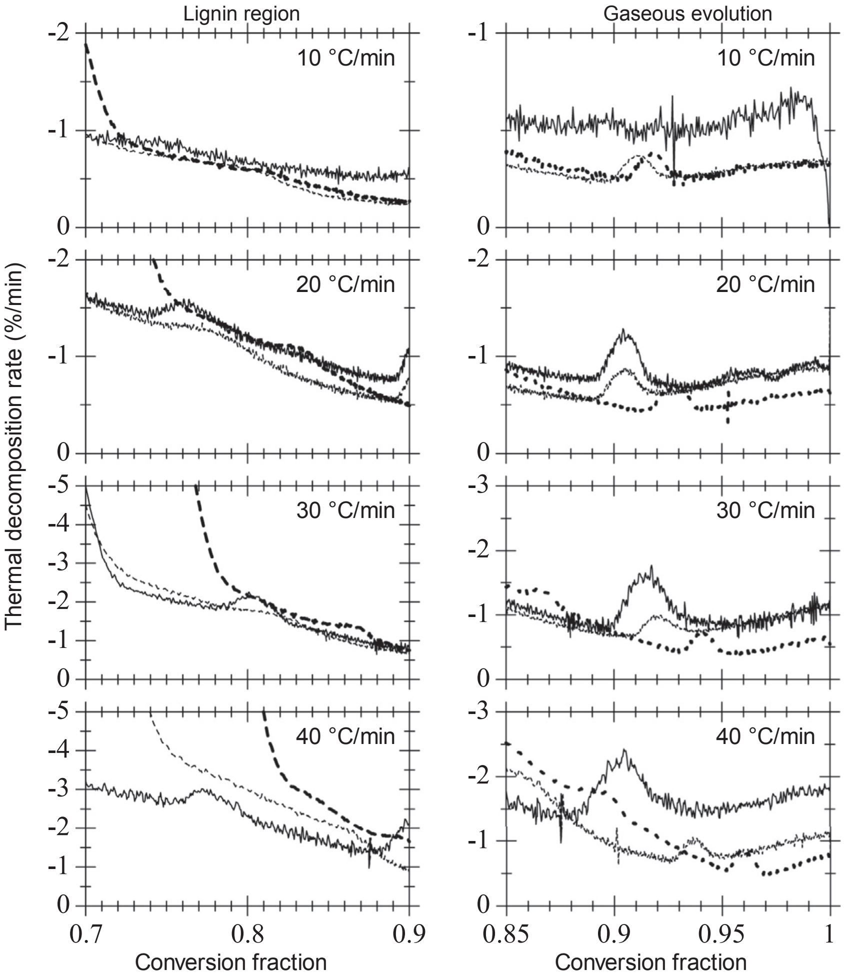

Fig. 3. Exploded view of regions of lignin degradation and gaseous evolution in wood (solid lines) and two types of briquettes (dark dashed lines are pigeon pea stalk briquettes and light dashed lines are soybean straw briquettes).

related to the release of methane and hydrogen. The evolution of these two gases is due to the secondary charring process occurring in the final stages of the thermal degradation. In case of wood there were two very dull peaks, at $\alpha = 0.89$ related to methane release and at $\alpha = 0.92$ related with hydrogen generation. At $\beta = 20$, 30, 40 °C/min, the peak related to gaseous evolution were sharp in wood. At the lower heating rate of 10 °C/min, the PB and SB showed the hydrogen related peak between two dull peaks in the case of wood. At 20 °C/min, the wood and SB showed similar peaks in the gaseous evolution region, whereas PB showed the peak at higher α-location. The sharp peaks (gaseous evolution) were at higher α-locations in case of briquettes at β of 30 and 40 °C/min as compared to wood. In thermogravimetric experiments on lignocellulosic biomaterial (Palm Kernel Shell), Idris et al., 2010 observed minor peaks in the range of 650–750 °C and slightly above 750 °C. In their thinking, these peaks were related to release of methane and hydrogen evolved during the charring process [33]. Idris et al., 2012 found TG-signals at relatively lower temperatures (~600 °C) for palm kernel shell (same lignocellulosic biomaterial) during TGA in combustion conditions ascribed to fixed carbon [34]. Present writing considers that the TG-peaks emerging above 600 °C (located in 700–750 °C) can reasonably be linked to release of CH_4 and H_2. The temperatures near 720 ± 10 °C and 750 ± 20 °C are more accurate indication of the release of CH_4 and H_2, respectively. Abdullah et al., 2010 stated that the peak at the higher temperature may be due to the charring of the lignin in their study on the pyrolysis of various lingocellulosic biomasses for potential hydrogen generation using the thermogravimetry [35]. The α-range associated with the temperature range 700–750 °C and higher, started after the α-value of 0.89.

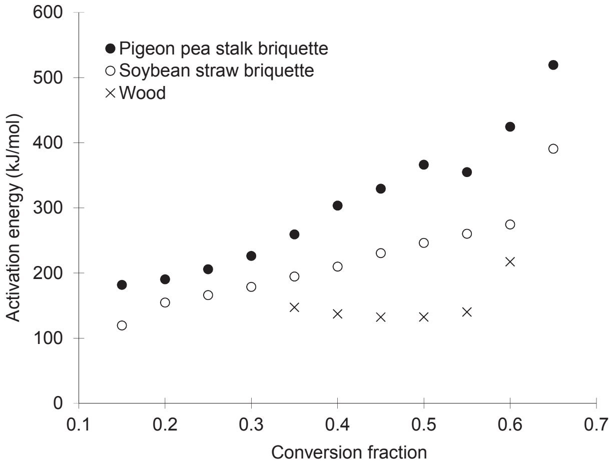

Fig. 4. Activation energy levels in the region of hemicellulosic and cellulosic bio-polymeric degradation showing that the energy levels of briquettes were more than wood, indicating better thermal stability of briquettes.

Table 1
OFW kinetic lines at different conversion fractions (α) for wood, soybean straw briquette and pigeon pea stalk briquette.

α	Wood		Soybean straw briquette		Pigeon pea stalk briquette	
	OFW kinetics lines	R^2	OFW kinetics lines	R^2	OFW kinetics lines	R^2
0.01	$y = -20785x + 66.812$	0.94	$y = -26129x + 81.09$	0.48[a]	$y = -12386x + 39.277$	0.95
0.05	$y = 1731.4x - 1.2491$	0.74[a]	$y = -14488x + 40.995$	0.82	$y = -8452.7x + 24.297$	0.91
0.10	$y = 4509.1x - 5.8266$	0.55[a]	$y = -8662.5x + 22.769$	0.85	$y = -17526x + 37.355$	0.76[a]
0.15	$y = 18189x - 30.087$	0.14[a]	$y = -15097x + 32.599$	0.83	$y = -22979x + 45.157$	0.97
0.20	$y = -24981x + 47.333$	0.32[a]	$y = -19556x + 39.525$	0.84	$y = -24053x + 46.004$	0.99
0.25	$y = -21182x + 39.76$	0.50[a]	$y = -20983x + 41.049$	0.88	$y = -26029x + 48.734$	0.99
0.30	$y = -19498x + 36.193$	0.66[a]	$y = -22587x + 43.023$	0.94	$y = -28599x + 52.524$	0.99
0.35	$y = -18611x + 34.108$	0.81	$y = -24593x + 45.783$	0.96	$y = -32798x + 59.078$	0.98
0.40	$y = -17353x + 31.59$	0.90	$y = -26526x + 48.4$	0.99	$y = -38385x + 67.84$	0.98
0.45	$y = -16716x + 30.209$	0.94	$y = -29146x + 52.18$	0.99	$y = -41654x + 72.592$	0.98
0.50	$y = -16767x + 30.013$	0.95	$y = -31130x + 54.87$	0.99	$y = -46331x + 79.691$	0.97
0.55	$y = -17729x + 31.272$	0.96	$y = -32921x + 57.247$	0.99	$y = -44901x + 76.688$	0.96
0.60	$y = -27479x + 46.202$	0.99	$y = -34730x + 59.585$	0.99	$y = -53697x + 90.387$	0.98
0.65	$y = 14718x - 19.371$	0.49[a]	$y = -49438x + 82.281$	0.84	$y = -65703x + 109.04$	0.96
0.70	$y = 8459.8x - 9.1658$	0.61[a]	$y = 13481x - 17.714$	0.38[a]	$y = 267625x - 423.28$	0.30[a]
0.75	$y = 8027.1x - 7.6314$	0.44[a]	$y = 7201.1x - 7.3141$	0.44[a]	$y = 13623x - 17.893$	0.99
0.80	$y = 9312.5x - 8.3242$	0.41[a]	$y = 6076.9x - 5.0002$	0.40[a]	$y = 6409.6x - 6.1693$	0.91
0.85	$y = 7935.3x - 5.6937$	0.21[a]	$y = 5320.8x - 3.2816$	0.43[a]	$y = 5572.1x - 4.2076$	0.88
0.90	$y = -5921.1x + 8.9226$	0.02[a]	$y = 6033.6x - 3.132$	0.50[a]	$y = 5177.5x - 2.7967$	0.85
0.95	$y = -21486x + 22.204$	0.20[a]	$y = 15400x - 10.633$	0.50[a]	$y = 8656x - 5.0977$	0.76[a]

Where; $y = \ln(\beta)$ and $x = 1/T$.

[a] The regression was not adequate for further OFW analysis.

Present article explains the presence of two close minor peaks at the higher conversion fraction (0.9–1.0) on the basis of bond energy of C–H and H–H. The presence of two peaks [20,21,33–35], at higher temperature regime, 700–750 °C and just above, in lignocellulosic biomaterials, can be understood considering the bond energies for C–H and H–H bonds. The bond energy of C–H (414 kJ/mol) is lower than H–H (436.4 kJ/mol) [36]. Therefore, the temperature regimes of release of methane and hydrogen must closely fall as the bond energies of C–H are close to H–H. Further, the hydrogen evolution should be at relatively higher α-value than the evolution of methane. Similarly, methane evolution should occur at slightly lower α-value than the hydrogen.

3.1. *Kinetics*

The activation energy profiles with respect to α for wood and two types of briquette are given in Fig. 4 using Ozawa-Flynn-wall (OFW). Fig. 4 highlights that the activation energies associated with hemicellulosic and cellulosic decomposition were higher in briquettes than these energies in wood. White et al. (2011) [15] and Tasmba et al. (2006) [37] mentioned the activation energies of various lignocellulosic biomaterials. The E-values obtained in this writing were in similar lines with other reporting [15,16,20,21,29–31]. The article states the finding that wood is thermally softer than the briquettes of loose lignocellulosic crop residues with regard to hemicellulosic and cellulosic decomposition. The lignin region could not be evaluated in the present article due to the limitations of the kinetics tool to obtain the better regression ($R^2 > 0.8$) for Ozawa-Flynn-Wall (OFW) isoconversional kinetics lines (Table 1) above $\alpha > 0.6$. Based on the OFW kinetics lines, the accelerating nature of the thermal decomposition process was until the α-values of 0.60, 0.65 and 0.65 for W, SB and PB, respectively. This showed that briquettes are more thermally harder biofuel than wood. After these values of α, the thermal decomposition process slowed and followed the retardation mode in respective biomaterials.

The biomatrix is highly complex as it has a large range of polymers. Vyazovkin and Sbirrazzuoli (2006) mentioned that the decomposition of organic polymer is a complex process wherein the decomposition cannot be explained in terms of molecular bonding energies [17]. They stated that decomposition of C–C bond might start well below the bonding energy of C–C (350 kJ/mol). Thermal decomposition can start at lower energy input to polymers due to weak link sites inherent in polymer chains [17]. The weak sites in polymers were considered as head-to-head links, hydroperoxy, and peroxy structures [17]. The degradation initiates at these weak locations and then the decomposition follows the radical pathways [17]. The average bond energies between the different elements (C, H, O, N, S) remain generally higher than the activation energy obtained in the kinetics of the biomaterial. However, the maximum values of activation energies of biomaterial cannot exceed the highest possible bonding energy of the most stable bond in biomatrix.

The existing knowledge mentions that the lignin plays an important role to bind the biocompounds to form the briquette. Present article claims that the contributions of intrinsic hemicellulosic and cellulosic biopolymers are also important, and the effects of these bioconstituents were proved as positive for the thermal stability function of briquetted biofuel.

4. Conclusions

The thermal stability of briquetted biofuel was proved higher than the wood on the basis of activation energy levels, especially for hemicellulose and cellulose. The present article found that intrinsic hemicellulosic and cellulosic biopolymers contributed positively towards the thermal stability of the briquetted biofuel. Therefore, during formation of briquette the intrinsic hemicellulosic and cellulosic biopolymers undergoes through changes which leads to higher thermal stability in briquette. Thermal stability levels of briquette may exceed the thermal stability levels of wood. The findings of this article change the general notion that wood is thermally stronger than the briquetted biofuel from loose crop residues. The present paper proves that the briquettes are relatively superior in terms of thermal strength of their biopolymeric constitution in comparison to wood. This is altogether a new fact to be informed of the scientific community.

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